

Age and source of different forms of carbon released from boreal peatland streams during spring snowmelt in E. Finland

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Abstract Isotopic data are increasingly being used to quantify and understand the processes that control the release of carbon (C) from northern peatlands. We used $\delta^{13}\text{C}$ and ^{14}C measurements to investigate the source and age of different forms of aquatic C (DOC, POC and evasion CO_2) released from 2 contrasting (undrained v drained) forested peatland catchments at the end of the winter snowmelt period in boreal E Finland. The $\delta^{13}\text{C}_{\text{VPDB}}$ values of DOC (range -28.3 to -28.8 ‰) were generally more ^{13}C depleted than evasion CO_2 (range -22.7 to -31.5 ‰) and showed no clear differences between the pre-flood, flood and post-flood periods. Both forms of C had evidence of bomb- ^{14}C (i.e. $>100\%$ modern), indicating that they contained substantial quantities of C fixed since the mid AD

1950s. However, DOC was ^{14}C enriched compared to evasion CO_2 , with ^{14}C concentrations suggesting that, on average, DOC-C was ~ 5 – 6 years younger than evasion CO_2 -C, with the most recently fixed C being released when temperatures were highest. POC was significantly depleted in ^{14}C with conventional (uncalibrated) radiocarbon ages of 805–1135 BP. In contrast to other studies, the isotopic compositions of DOC and evasion CO_2 were very similar, suggesting a predominantly single and consistent C source (decomposition of soil organic matter; SOM) during the snowmelt period. Whilst we found no evidence to suggest that old (pre-bomb) C was being released at the end of the winter period, the drained site was associated with more ^{14}C depleted and ^{13}C enriched evasion CO_2 , suggesting a closer link to the atmospheric CO_2 pool. Our isotopic data suggest that the various forms of C released to the aquatic system from these forested Finnish peatlands are closely related, largely unaffected by drainage and (at least in the case of evasion CO_2 and DOC) indicate strong connectivity between C cycling in the soil–plant–water system.

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Introduction

The stability of the northern peatland C store and its ability to continue to sequester C from the

atmosphere on a year-on-year basis will have significant long-term impact on the global C cycle (Gorham 1991). The boreal regions (of which Finland is a part) are predicted to show some of the greatest impacts of global warming (e.g. Serreze et al. 2000) and there is concern that these important long-term C stores are becoming unstable in response to climate and land-use change, with predictions of significant release of “old” (pre-bomb) soil C in both gaseous and dissolved forms (Frey and Smith 2005; Guo and MacDonald 2006). The suggestion that the disappearance of permafrost will result in increased DOC (dissolved organic carbon), CO₂ and CH₄ release from peatlands (Walter et al. 2006; Mastepanov et al. 2008; Walter et al. 2008; Balcarczyk et al. 2009) has recently been supported by evidence from Alaska (Schuur et al. 2009), although earlier studies found no evidence for this (Striegl et al. 2005; Raymond et al. 2007).

One of the most significant effects of climate change in these regions is likely to be in the timing and magnitude of the spring flood associated with melting of the winter snow pack. In the northern hemisphere the period of snow cover has decreased and the timing of lake and river ice breakup advanced by ~6.5 days per century (Lemke et al. 2007). The spring snowmelt event dominates the hydrological year and results in 50–66% of the annual runoff occurring during a relatively short (4–6 weeks) period of time (Kortelainen et al. 1997; Laudon et al. 2004). In countries with large soil C stores like Finland (where peatlands cover ~30% of the land area and store ~5960 million tonnes of C; Turunen 2008), this results in significant annual losses of aquatic C (Dyson et al. 2011). A major spring “carbon export event” has been observed in other countries such as Sweden and the USA (Laudon et al. 2004; Striegl et al. 2007). The spring snowmelt period is also associated with significant degassing of CO₂ and CH₄ to the atmosphere from melting lakes in peatland landscapes (Striegl and Michmerhuize 1998; Juutinen et al. 2009). Although $\delta^{13}\text{C}$ measurements beneath the ice of boreal lakes indicate a respiration source for this CO₂ (Striegl et al. 2001), relatively little is known about the origin of C (in its various forms) associated with the spring flood event in boreal peatlands. One exception is the work of Raymond et al. (2007) who found that during the spring thaw 90% of DOC exported in the largest arctic rivers was

1–20 years old, with the largest single component being 1–5 years old.

Isotopic (¹³C and ¹⁴C) analysis therefore provides a powerful tool to both source and age different aquatic C species (Palmer et al. 2001; Raymond and Bauer 2001a; Mayorga et al. 2005). Research consistently suggests that most of the DOC lost from peatlands and organic soils is modern (Benner et al. 2004; Evans et al. 2007), although recent data from the Yukon and Tanana Rivers in N America (Striegl et al. 2007) has shown the presence of DOC up to 497 years BP. Methane released from thawing permafrost along the margins of Siberian lakes has been dated to be of Pleistocene age (35–43,000 years BP) (Walter et al. 2006). Peat pore waters are known to contain DOC that is consistently younger than the surrounding peat, with radiocarbon ages ranging from modern to 6900 years BP (Charman et al. 1999; Chasar et al. 2000; Palmer et al. 2001; Clymo and Bryant 2008). The age of gaseous C trapped in peat is known to increase with increasing depth with ages up to 4300 years BP for CO₂ and 3960 years BP for CH₄ (Charman et al. 1999; Chasar et al. 2000; Clymo and Bryant 2008). The peat profile therefore contains old pre-bomb C, which if detected in the aquatic system would provide evidence of linkage to deep peat C stores.

The examples above show that the isotopic composition of C transported in streams and rivers depends largely on its form. Whilst terrestrial DOC transported to rivers and lakes is ¹⁴C enriched and largely derived from C fixed since the AD 1963 bomb peak (Hedges et al. 1986), POC is typically significantly depleted in radiocarbon with ages varying from 100's to 1000's of years BP. The rare occurrence of ¹⁴C depleted DOC in rivers is likely caused by anthropogenic disturbance, periods of drought leading to water table drawdown and preferential decomposition of young DOC (but not old ¹⁴C depleted DOC) in the aquatic system (Schiff et al. 1997; Raymond and Bauer 2001b; Evans et al. 2007). The variable $\delta^{13}\text{C}$ values of DIC in streams and rivers implies that it originates from biogenic (primarily allochthonous SOM), geogenic (deep weathering) and atmospheric sources (Striegl et al. 2001, 2007; Mayorga et al. 2005). In a study of DOC and CO₂ released from UK peatlands, Billett et al. (2007) found a significant difference between the isotopic signature of DOC and CO₂ lost by evasion from surface waters. The isotopic values of CO₂ were highly variable

compared to DOC, indicating that CO₂ derived from peatlands varied widely in terms of source and age. In addition, the results indicate that CO₂-C and DOC-C released from peatlands are to some extent decoupled, suggesting that the control mechanisms (hydrological vs. biogeochemical) and sources (biogenic vs. geogenic) are different.

Whilst the emphasis on radiocarbon dating of the aquatic system has understandably focused on large river systems like the arctic rivers (Raymond et al. 2007) and the Amazon (Mayorga et al. 2005), the interpretation of the isotopic data is more difficult due to their size and complexity. Isotopic measurements in smaller catchments are needed to better understand the links between the cycling of C in the soil-plant-water system. Here we use a dual isotope ($\delta^{13}\text{C}$ and ^{14}C) approach to measure the source and age of CO₂, DOC and POC released to the aquatic system during the spring snowmelt period in 2 contrasting (undrained and drained) forested peatland catchments in E Finland. Drainage has a significant impact on peatland hydrology in countries like Finland where ~35% of forests are located on peatlands and about half are drained (Finnish Statistical Yearbook of Forestry 2009). Our study is not limited to a specific C species such as DOC, and to our knowledge this is the first time that ^{14}C measurements have been made from headwater streams in forested peatlands. In addition, evasion CO₂ has never been measured directly over the spring snowmelt period.

We hypothesised that (i) winter freezing switches off near-surface turnover of recently fixed C and old trapped soil derived C is released into drainage systems before the spring snowmelt period, (ii) spring runoff is dominated by near-surface flow associated with recently fixed carbon and (iii) peatland drainage has the potential to “tap” old soil C which is released in the form of CO₂, DOC and POC. To test these hypotheses we combined intensive monitoring of the outlets of the study catchments in E Finland during the spring snowmelt event (Dyson et al. 2011; Dinsmore et al. in press), with a series of isotopic measurements timed to coincide with the pre-flood, flood and post-flood periods.

Study sites

The 2 study catchments, Vällipuro (0.86 km²) and Suopuro (1.13 km²), are located next to each other in

the North Karelia region of E Finland (63°52'N, 28°39'E). They are both forested (dominantly *Picea abies* and *Pinus sylvestris*) and lie at an elevation of 200–220 m amsl. Peat (2.5–3.2 m depth) dominates both catchments (Vällipuro 56%, Suopuro 70%) which are developed on base poor parent material (Ahtiainen et al. 1988). Vällipuro is undrained (the control site), whereas 13% of the lowermost part of the Suopuro catchment (the drained site) was ditched in 1983. A small part of both catchments (<10% of the catchment area) was clear-cut during the period 1999–2001. Mean annual precipitation and temperature is 612 mm and 1.5°C respectively, with typically 5–6 months (October–March) of snow cover each year. Neither of the sites contain areas of permafrost. Both study sites form part of a long-term research programme (started 1979) to study the effects of forestry practices on water quality (Ahtiainen et al. 1988; Latja and Kurimo 1988; Kortelainen et al. 2006; Sarkkola et al. 2009; Rantakari et al. 2010). For a more detailed description of the catchment characteristics see Dyson et al. (2011).

Differences in mean discharge over the sampling period reflected differences in catchment size (Table 1). Streamwater chemistry was characterised by acidic, organic-rich runoff, with the Vällipuro catchment characterised by higher mean concentrations of DOC, POC, free CO₂-C and DIC (Table 1).

Methods

Between 7th April–1st June 2008 we carried out an intensive monitoring programme of C concentrations

Table 1 General site and streamwater characteristics of the Vällipuro (undrained) and Suopuro (drained) catchments during the spring 2008 snowmelt period (after Dyson et al. 2011)

	Vällipuro	Suopuro
Area (km ²)	0.86	1.13
% drainage	0	13
Mean discharge (l s ⁻¹)	44.3	51.0
Mean pH	4.25	4.13
Mean DOC (mg l ⁻¹)	26.2	17.5
Mean POC (mg l ⁻¹)	0.88	0.82
Mean CO ₂ -C (mg l ⁻¹)	2.97	2.70
Mean DIC (mg l ⁻¹)	3.07	1.22

and flux measurements at the outlets of both catchments using a combination of continuous sensors and spot sampling (Dyson et al. 2011). Here we use the C concentration and discharge data as a framework to interpret the $\delta^{13}\text{C}$ and ^{14}C measurements.

On 8 separate occasions over the study period DOC, POC and evasion CO_2 samples were collected for isotopic analysis of $\delta^{13}\text{C}$ and ^{14}C . Two samples were collected before, 4 during and 2 after the peak snowmelt discharge period. Sampling for DOC and POC involved collection of a 1 L streamwater sample in an acid washed glass Schott bottle. The sample was filtered on the day of collection through a pre-ashed (500°C for 3 h) 0.7 μm (GFF) filter and the POC washed off the filter into a glass vial. The POC sample was stored at 4°C in the dark until analysis at the NERC Radiocarbon Facility (NERC RCF) at East Kilbride (UK). The filtrate was transferred back into the 1 L bottle ready for DOC analysis at the NERC RCF.

DOC samples were acidified to pH 4 by addition of 2 M HCl and sparged by bubbling with nitrogen gas for 20 min. Sample acidity was then adjusted to just below pH 7 by addition of freshly prepared 1 M KOH, and measured volumes of the samples were rotary evaporated in acid-washed glassware until a few ml of solution remained, and then freeze dried. To remove potential traces of carbonate, POC samples were soaked overnight in 0.5 M HCl. The POC samples were then rinsed with deionised water, dried and homogenised. The dried DOC and POC samples were combusted (900°C) using the sealed quartz tube method (Boutton et al. 1983) and sample CO_2 recovered by cryogenic trapping.

CO_2 lost by evasion from the water surface was collected directly using a water tight opaque floating chamber connected to a portable zeolite molecular sieve CO_2 sampling system (Hardie et al. 2005; Billett et al. 2006). Sampling time is a function of evasion rate (calculated as the rate of change of CO_2 concentration over a 10 min period), but typically it takes 2 h to scrub, accumulate and then trap sufficient CO_2 (~5–15 ml) for AMS ^{14}C analysis. The sampling system firstly purges atmospheric CO_2 from the floating headspace, secondly allows build up of CO_2 in the chamber headspace and finally, after sufficient CO_2 has evaded and accumulated in the chamber, traps the gas using a cartridge containing zeolite molecular sieve (type 13X). Before purging atmospheric CO_2 in the chamber, evasion rate was measured using the

relationship between time, concentration, chamber area and volume (Billett and Moore 2008). Potential atmospheric contamination of the final sample (estimated to be <1%) is minimised by scrubbing 4 chamber volumes of air prior to trapping (Billett et al. 2007). After trapping the evaded CO_2 , the molecular sieve cartridges were returned to the NERC RCF and the CO_2 recovered by heating (500°C) and cryogenic trapping (see Hardie et al. 2005).

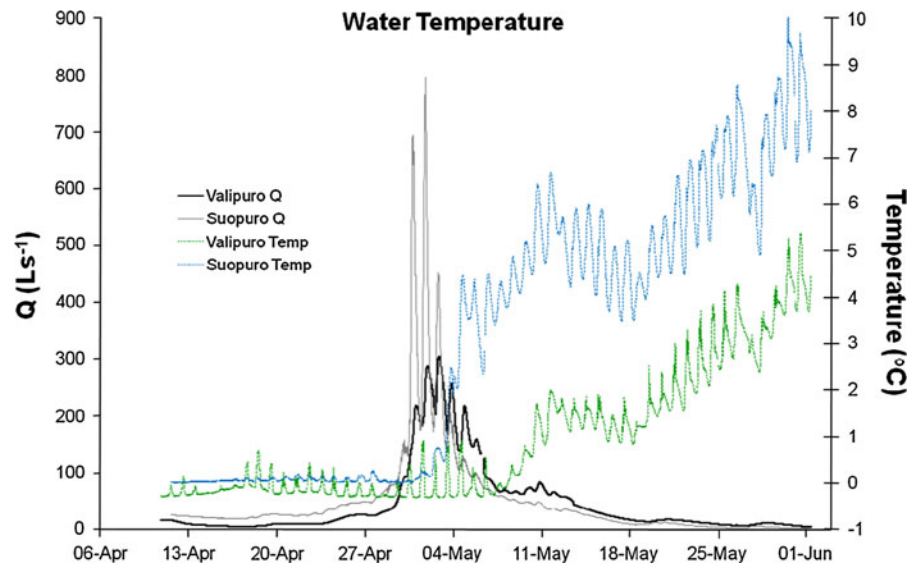
Carbon dioxide derived from the DOC, POC and evasion samples was split into separate aliquots for $\delta^{13}\text{C}$ and ^{14}C analysis. $\delta^{13}\text{C}$ values ($^{13}\text{C}/^{12}\text{C}$ ratio in ‰ units relative to the standard Vienna Pee Dee Belemnite; VPDB) were determined using a dual inlet isotope ratio mass spectrometer (VG Optima, Micromass, UK). The ^{14}C aliquot of sample CO_2 was converted to graphite by Fe–Zn reduction (Slota et al. 1987) and analysed on an accelerator mass spectrometer (AMS) at the Scottish Universities Environmental Research Centre (SUERC), East Kilbride, UK (Freeman et al. 2007). ^{14}C results were normalised to a $\delta^{13}\text{C}$ value of –25‰ to account for mass-dependant fractionation, and expressed as conventional radiocarbon ages (years BP) and ‰modern (Stuiver and Polach 1977). Following convention, measurement uncertainties associated with isotope concentrations are expressed as standard deviations. Only 2 of the samples contained sufficient C for ^{14}C analysis of POC. These were collected from the Välipuro catchment and coincided with the highest flows and highest measured POC concentrations.

For evasion CO_2 the measured isotopic values were corrected to account for the fact that the CO_2 collected in the chamber had not fluxed out directly into the free atmosphere, but into a chamber atmosphere with a higher CO_2 concentration. The correction, which is discussed in detail in Billett and Garnett (2010) and accounts for isotopic fractionation across the air–water interface in the collection chamber, uses measured water temperature, pH and DIC concentration values to determine the isotopic composition of the evasion CO_2 that would have fluxed out into a contemporary free atmosphere.

Results

Stream discharge increased significantly in both catchments during the 2008 snowmelt period from

Fig. 1 Changes in stream discharge (Q) and water temperature at the Vällipuro (*undrained*) and Suopuro (*drained*) catchments during the spring 2008 snowmelt event



pre-flood minima of 5 and 19 l s^{-1} to flood maxima of 287 and 796 l s^{-1} in the Vällipuro and Suopuro catchments, respectively (Fig. 1). After the period of peak flow stream temperatures recovered more rapidly in Suopuro than Vällipuro; this also coincided with a rise in magnitude of the diurnal temperature signal.

Streamwater DOC concentrations were consistently higher in Vällipuro compared to Suopuro, with both streams showing a decrease in concentration during the period of highest flows, followed by a gradual recovery in concentration on the receding limb of the hydrograph (Fig. 2a). Temporal changes in CO_2 concentration showed a similar pattern (Fig. 2b), although there was no evidence of a recovery in concentration in the Suopuro catchment, 30 days after the peak flow period. Concentrations of POC were low (0.3–1.7 mg l^{-1}) throughout the study period, although the patterns of change were consistent in both catchments (Fig. 2c) with several increases/decreases in concentration. Highest POC concentrations occurred in Vällipuro and were associated with the peak discharge period.

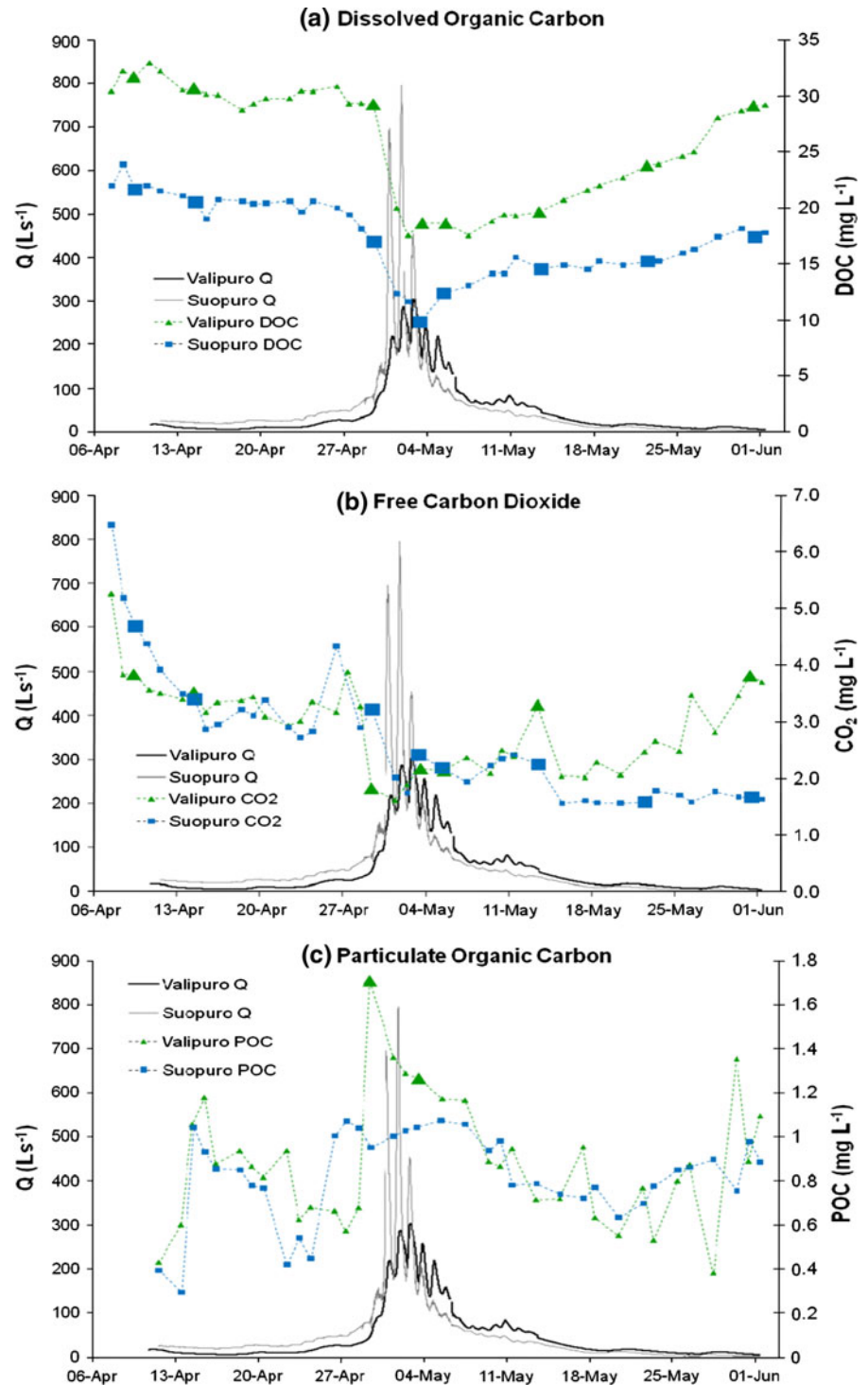
Instantaneous DOC and CO_2 evasion fluxes determined at the same time as the 8 isotopic measurements, showed contrasting changes over the study period (Fig. 3). Evasion rates were highest during the baseflow period at the beginning of the study, lowest during the peak flow period and then increased (particularly in Vällipuro) on the receding limb of the

flood hydrograph. In contrast, instantaneous fluxes of DOC were highest when stream discharge was highest.

The $\delta^{13}\text{C}$ values of DOC lost in runoff from both catchments were similar ($t = 1.82$; $P = 0.11$) and varied from -28.3 to -28.8 (Vällipuro) and -28.3 to -28.6 (Suopuro), with no temporal change during the study period (Table 2; Fig 4a). However, evasion $\delta^{13}\text{C}\text{-CO}_2$ values were consistently more ^{13}C enriched in Suopuro (-22.7 to -27.1) compared to Vällipuro (-24.6 to -31.5) with a similar pattern of change in both catchments (Table 3; Fig 4a). The differences in evasion $\delta^{13}\text{C}\text{-CO}_2$ between the 2 catchments were statistically significant ($t = 6.06$; $P = 0.001$). The most negative (^{13}C depleted) evasion $\delta^{13}\text{C}\text{-CO}_2$ values were found at the same time in both catchments (14 April 2008) at low stream flow before the onset of the main spring snowmelt period. Overall, evasion CO_2 was significantly more ^{13}C enriched compared to DOC in both catchments (Vällipuro $t = 3.18$, $P = 0.015$; Suopuro $t = 16.28$ $P = <0.001$).

With the exception of one sampling date (29 April 2008) associated with the rising limb of the snowmelt hydrograph, streamwater DOC was significantly ($t = 2.52$; $P = 0.039$) more ^{14}C enriched in Vällipuro compared to Suopuro Fig. 4b). Whilst $^{14}\text{C}\text{-DOC}$ values were relatively consistent during the course of the study (110.41–112.56%modern), on the final sampling occasion (31 May 2008) both

Fig. 2 Changes in **a** DOC, **b** free CO_2 and **c** POC and stream discharge (Q) in Vällipuro and Suopuro during the spring 2008 snowmelt event (after Dyson et al. 2011). The large symbols signify the time at which samples were collected for isotopic measurements



streams exhibited their least ^{14}C -enriched DOC values (Vällipuro 110.64%modern; Suopuro 107.31%modern). In contrast to the radiocarbon age of DOC

(which were all >100%modern; i.e. indicating a substantial post AD 1950/60s component), the 2 POC samples collected from Vällipuro during the

Fig. 3 Instantaneous CO₂ evasion and DOC fluxes at the time when the samples for isotopic ($\delta^{13}\text{C}$ and ^{14}C) analysis were collected

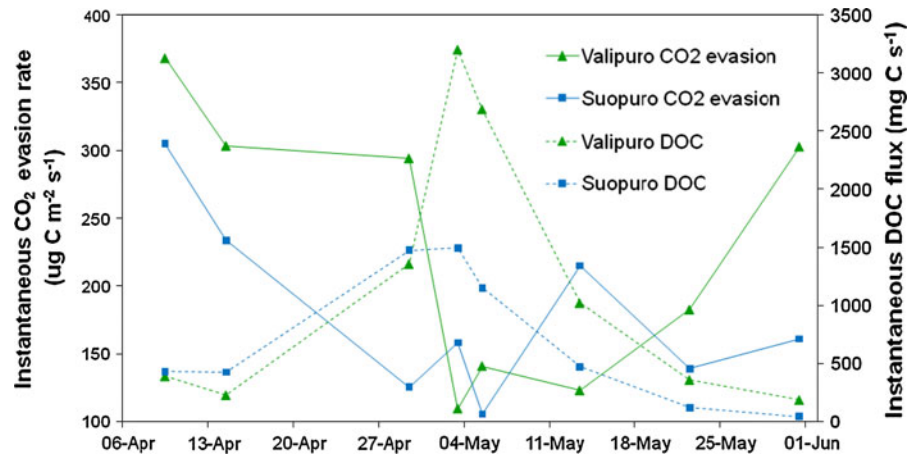


Table 2 Isotopic characteristics of DOC and POC collected during the 2008 spring snowmelt event

Site	Date (dd/mm/yy)	Carbon species	Publication code	$\delta^{13}\text{C}_{\text{VPDB}}\text{‰}$ (± 0.1)	^{14}C Enrichment (%Modern $\pm 1\sigma$)
Välipuro	09/04/2008	DOC	SUERC-20142	-28.3	111.91 \pm 0.51
Välipuro	14/04/2008	DOC	SUERC-20140	-28.3	112.56 \pm 0.51
Välipuro	29/04/2008	DOC	SUERC-20155	-28.8	111.11 \pm 0.48
Välipuro	03/05/2008	DOC	SUERC-20137	-28.5	112.16 \pm 0.49
Välipuro	05/05/2008	DOC	SUERC-20136	-28.4	111.76 \pm 0.51
Välipuro	13/05/2008	DOC	SUERC-20152	-28.6	111.78 \pm 0.49
Välipuro	22/05/2008	DOC	SUERC-20154	-28.4	111.81 \pm 0.51
Välipuro	31/05/2008	DOC	SUERC-20143	-28.5	110.64 \pm 0.51
Välipuro	29/04/2008	POC	SUERC-20039	-29.6	90.47 \pm 0.28 ^a
Välipuro	03/05/2008	POC	SUERC-20038	-31.0	86.83 \pm 0.25 ^b
Suopuro	09/04/2008	DOC	SUERC-20151	-28.3	111.59 \pm 0.49
Suopuro	14/04/2008	DOC	SUERC-20141	-28.3	110.41 \pm 0.50
Suopuro	29/04/2008	DOC	SUERC-20153	-28.6	111.50 \pm 0.51
Suopuro	03/05/2008	DOC	SUERC-20144	-28.5	110.74 \pm 0.51
Suopuro	05/05/2008	DOC	SUERC-20147	-28.3	110.90 \pm 0.51
Suopuro	13/05/2008	DOC	SUERC-20146	-28.3	110.41 \pm 0.51
Suopuro	22/05/2008	DOC	SUERC-20150	-28.5	111.06 \pm 0.51
Suopuro	31/05/2008	DOC	SUERC-20145	-28.3	107.31 \pm 0.49

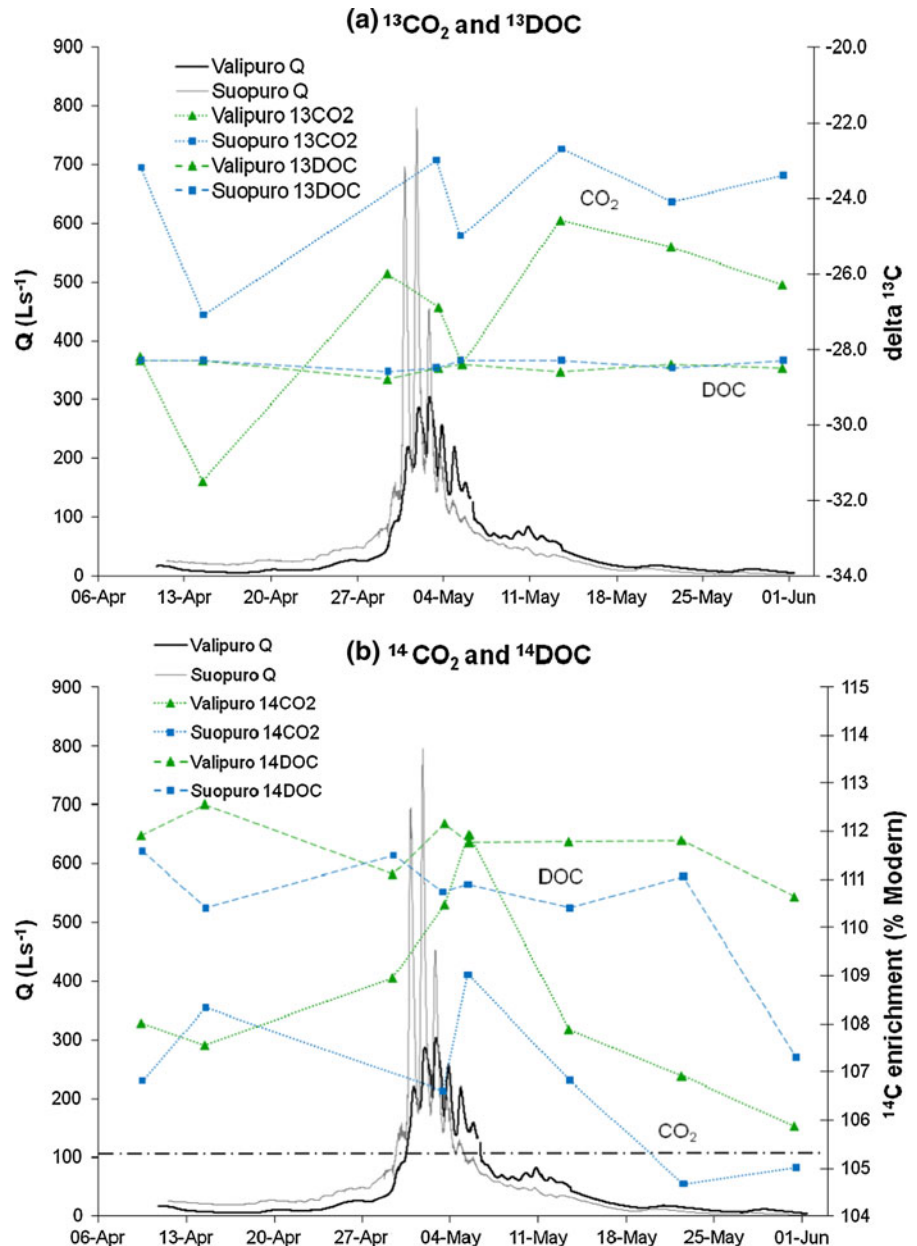
Conventional radiocarbon age (years BP $\pm 1\sigma$) for the two POC samples are ^a 805 \pm 35, ^b 1135 \pm 35 years BP

period of peak spring stream flows, were significantly more ^{14}C depleted, with conventional radiocarbon ages of 805 and 1135 years BP (Table 2).

With the exception of 5 May 2008 (when values in Välipuro were similar), DOC was significantly more ^{14}C enriched compared to evasion CO₂ at both sites (Välipuro $t = 5.04$, $P = 0.001$; Suopuro $t = 6.77$, $P = 0.001$). In Välipuro evasion ^{14}C -CO₂ values were

initially 107.5–108.0, became more ^{14}C enriched as flow increased over the snowmelt period (with greatest enrichment just after peak flow) and then decreased on the receding limb. In Välipuro the least ^{14}C enriched CO₂ evasion value occurred at the end of the sampling period; Suopuro showed no clear trend over time. In both sites the least ^{14}C enriched evasion values were measured at the end of the study period. Overall,

Fig. 4 Changes in **a** evaded $\delta^{13}\text{C}$ - CO_2 and $\delta^{13}\text{C}$ -DOC and **b** evaded $\delta^{14}\text{C}$ - CO_2 and $\delta^{14}\text{C}$ -DOC and stream discharge (Q) in Välipuro and Suopuro during the spring 2008 snowmelt event. The contemporary atmospheric ^{14}C concentration in 2008 (105.2%modern) is shown in **b** by a horizontal dashed line



evasion CO_2 was significantly more enriched in ^{14}C in Välipuro compared to Suopuro ($t = 4.49$; $P = 0.004$). We also found that the radiocarbon ages of DOC ($R^2 = 0.78$; $P = 0.049$) and evasion CO_2 ($R^2 = 0.73$; $P = 0.014$) were significantly correlated between the 2 streams (see also Fig. 4). Finally, stream flow was strongly and positively correlated with evasion $^{14}\text{CO}_2$ in Välipuro ($R^2 = 0.78$; $P = 0.008$); all other isotopic values were unrelated to flow.

Discussion

Interpretation of the snowmelt isotopic data

We used a dual isotope approach ($\delta^{13}\text{C}$ and ^{14}C) to investigate how the age and source of different forms of C released into streams draining two contrasting forested peatland catchments in E Finland varied during the 2008 spring snowmelt event. In a linked

Table 3 Isotopic characteristics of evaded CO₂ collected during the 2008 spring snowmelt event. The correction to account for isotopic fractionation across the air–water interface is described in Billett and Garnett (2010)

Site	Date (dd/mm/yy)	Carbon species	Publication code	Chamber-measured evasion $\delta^{13}\text{C}\text{-CO}_2 \pm 0.1 \text{ ‰}$		¹⁴ C Enrichment (%Modern $\pm 1\sigma$)	
				Original (a)	Gas flux method (b)	Original (a)	Gas Flux Method (b)
Välipuro	09/04/2008	CO ₂	SUERC-19512	−24.5	−28.2	105.80 \pm 0.49	108.02
Välipuro	14/04/2008	CO ₂	SUERC-19508	−24.6	−31.5	105.01 \pm 0.49	107.56
Välipuro	29/04/2008	CO ₂	SUERC-19525	−24.0	−26.0	107.54 \pm 0.50	108.96
Välipuro	03/05/2008	CO ₂	SUERC-19507	−22.1	−26.9	107.73 \pm 0.48	110.48
Välipuro	05/05/2008	CO ₂	SUERC-19506	−21.2	−28.4	107.89 \pm 0.51	111.93
Välipuro	13/05/2008	CO ₂	SUERC-19522	−22.7	−24.6	106.99 \pm 0.50	107.89
Välipuro	22/05/2008	CO ₂	SUERC-19524	−23.9	−25.3	106.32 \pm 0.46	106.91
Välipuro	31/05/2008	CO ₂	SUERC-19513	−24.4	−26.3	105.17 \pm 0.49	105.88
Suopuro	09/04/2008	CO ₂	SUERC-19519	−19.9	−23.2	104.87 \pm 0.49	106.81
Suopuro	14/04/2008	CO ₂	SUERC-19509	−21.3	−27.1	105.71 \pm 0.46	108.33
Suopuro	29/04/2008	CO ₂	SUERC-19523	−21.8	−57.2*	106.63 \pm 0.50	123.36*
Suopuro	03/05/2008	CO ₂	SUERC-19514	−19.1	−23.0	105.22 \pm 0.46	106.61
Suopuro	05/05/2008	CO ₂	SUERC-19517	−21.0	−25.0	107.07 \pm 0.50	109.02
Suopuro	13/05/2008	CO ₂	SUERC-19516	−19.1	−22.7	105.13 \pm 0.46	106.82
Suopuro	22/05/2008	CO ₂	SUERC-19518	−19.4	−24.1	103.68 \pm 0.48	104.68
Suopuro	31/05/2008	CO ₂	SUERC-19515	−20.4	−23.4	104.29 \pm 0.48	105.02

* Corrected value unrealistic and omitted henceforth

study cation concentrations were used as natural tracers to perform hydrograph separation at the same sites (Dinsmore et al. in press). The authors concluded that pre-event dissolved CO₂ and DOC originated from a common peat/groundwater source and up to ~40% of total downstream CO₂ export during the spring snowmelt period was directly from CO₂ trapped in air spaces in the snow pack, the remainder derived directly from soil storage.

The stable isotope data show that evasion CO₂ was more ¹³C enriched than both DOC and POC and more variable over the 2 month period. Like other studies (e.g. Billett et al. 2007; Clymo and Bryant 2008) the $\delta^{13}\text{C}$ value of DOC was consistent with dissolved organic matter (DOM) derived from C3 plants. Whilst most evasion CO₂ originates from C3 plants, a small degree of ¹³C enrichment suggested an additional contribution from either an atmospheric ($\delta^{13}\text{C} = \sim -8 \text{ ‰}$), weathering ($\delta^{13}\text{C} = \sim 0 \text{ ‰}$) or anaerobic fermentation ($\delta^{13}\text{C} = \sim -14$ to $+10 \text{ ‰}$) source (Billett et al. 2007; Waldron et al. 1999). CO₂ derived from methane oxidation would be expected to be very depleted in ¹³C (e.g. $\delta^{13}\text{C}$ methane

typically ~ -60 to -70 ‰ ; e.g. Clymo and Bryant 2008) and therefore there is little evidence in our results for a contribution via this pathway, except perhaps in the one sample with a $\delta^{13}\text{C}$ of -31.5 ‰ (Table 3).

Dinsmore et al. (in press) identified snowmelt CO₂ as a significant CO₂ source and in both catchments we consistently measured elevated (with respect to the atmosphere) CO₂ concentrations in the snowpack (Dyson et al. 2011), suggesting that an active deep microbial community exists under the snowpack. Bowling et al. (2009) measured snowpack $\delta^{13}\text{C}\text{-CO}_2$ values ranging from -22 to -8 ‰ , with differences over time being associated with both diffusive transport of CO₂ within the snowpack and external physical factors such as changes in wind speed and/or air pressure. In our study, although there was not a distinct “pulse” of ¹³C enriched CO₂ associated with the spring flood event, during the 2 month period $\delta^{13}\text{C}\text{-CO}_2$ did vary from -31.5 to -24.6 ‰ , suggesting that the relative contribution of different CO₂ sources changed over time. This might reflect variation in the relative amounts of

atmospheric (^{13}C depleted) CO_2 in the evasion signal over a period when the aquatic system is “reconnecting” with the atmosphere as the snow pack disappears. The relative consistency in the stable isotope signal from the 2 study catchments contrasts to lake systems, where the $\delta^{13}\text{C}$ value of dissolved CO_2 during the spring snowmelt period is known to vary significantly (e.g. -26 to $+1\%$), the variation attributed to multiple CO_2 sources such as respiration, atmospheric mixing and weathering (Striegl et al. 2001).

The $\delta^{13}\text{C}$ values of the 2 POC samples (-29.6 and -31.0%) were slightly ^{13}C depleted compared to DOC. Whilst it is known that photosynthetic discrimination in C3 plants leads to variation in $\delta^{13}\text{C}$, with whole forest respiration values ranging from -30 to -24 (Bowling et al. 2008), the results are again consistent with SOM derived from C3 plants.

The ^{14}C data for DOC and evasion CO_2 were all $>100\%$ modern and therefore unambiguously show the incorporation of at least some bomb- ^{14}C (the samples contained at least a proportion of C fixed since $\sim\text{AD } 1957$ when atmospheric ^{14}C levels first exceeded 100% modern). However, we cannot exclude the possibility that some of the samples contained pre-bomb C, particularly since the DOC and evasion CO_2 were likely to have been derived from C of a range of ages. Whilst recognising that a definitive interpretation of the radiocarbon data is not possible, we interpret the ^{14}C results by making the simplifying assumption that all C in the DOC and evasion CO_2 samples was originally fixed after the AD 1963 atmospheric bomb- ^{14}C peak. This can be justified since all ^{14}C values for DOC and evasion CO_2 were either within measurement error, or consistently more ^{14}C -enriched than the contemporary atmosphere in the year of sampling (estimated to be $\sim 105.2\%$ modern in 2008 by extrapolating the records of Levin et al. (2008)). Thus, no sample provided definitive evidence for a component of pre-bomb C. Using this interpretation framework (see also Garnett and Stevenson 2004), the more ^{14}C enriched samples would be the oldest, with increasingly ^{14}C depleted samples becoming progressively younger, and samples containing contemporary carbon (AD 2008) having a ^{14}C concentration of $\sim 105.2\%$ modern.

For most of the study (the first 7 samples) the C associated with DOC released in the 2 streams was an

average of 111% modern implying a mean age of $\sim\text{AD } 1996$, with the youngest DOC measured at the end of the sampling period, particularly in the drained site (107% modern, $\sim\text{AD } 2004$). Hence there was no effect of the spring flood event on DOC age and no evidence of either “old” (pre-bomb) DOC being stored during, and released after, the winter freeze or being preferentially released from the drained site. Our results from E Finland are therefore consistent with those of Raymond et al. (2007), who found that DOC released in major arctic rivers during the spring snowmelt was dominated by recently fixed (1–20 year old) carbon. In contrast, and recognising that our data are limited to 2 samples collected during peak discharge, POC lost from the undrained site (Välipuro) was significantly depleted in ^{14}C , with radiocarbon ages of 805–1135 years BP. Aged (pre-bomb) POC has consistently been measured from high latitude rivers (Goni et al. 2005; Striegl et al. 2007). Although we did not measure ^{14}C in the peat profile, it is likely that POC in the Finnish catchments originates from deeper within the peat profile, possibly associated with reworked bank or stream sediments.

It was notable that DOC was least ^{14}C enriched at both sites on the final sampling occasion (31 May). This suggests that in the final sample there was either (i) an increased proportion of younger carbon in the DOC, or (ii) greater contributions of older (pre-bomb) C in the DOC. We consider the former to be the most likely explanation, since $\%$ modern values for DOC were still enriched relative to the contemporary atmosphere (therefore not providing definitive evidence for pre-bomb C). Since the $\delta^{13}\text{C}$ -DOC values in the final samples were identical to the earlier ones, the results suggest that the source for this more recent C was similar, i.e. SOM derived from C3 plants. The decrease in $\%$ modern values could reflect new or a greater contribution from contemporary plant exudates due to increasing plant photosynthetic activity linked to the progressive warming of surface soils in late spring.

Variation in the ^{14}C content of evasion CO_2 was greater than DOC and changed from 108 to 112 to 105% modern over the study period in the undrained site with a smaller change in the drained site. Using the same interpretation framework as for DOC (i.e. that all C was originally fixed after the AD 1963 bomb- ^{14}C peak), the average year of initial C fixation of evasion CO_2 therefore changed from $\sim\text{AD } 2002$

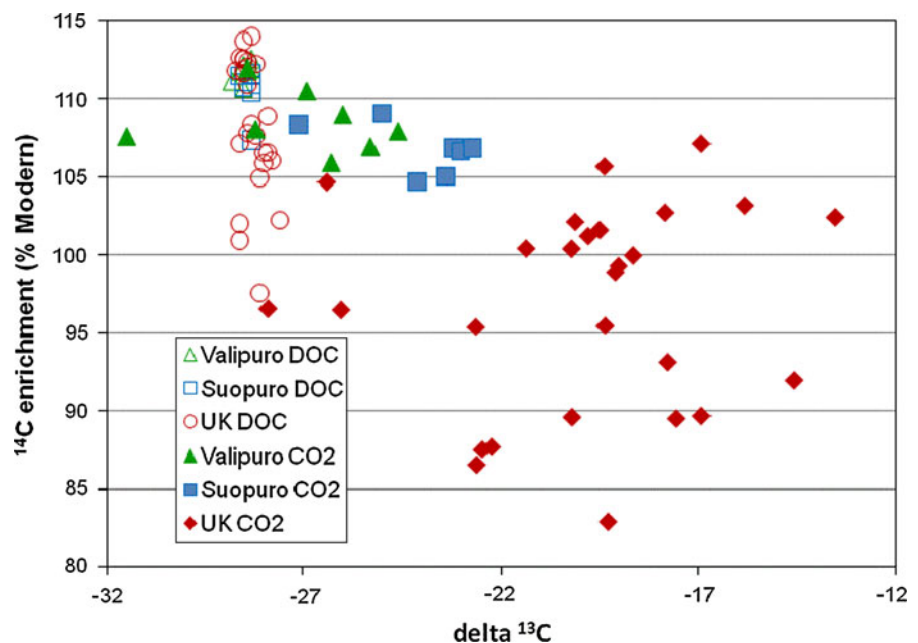
(pre-flood), to AD 1995 (flood) to AD 2008 (post-flood). This implies that (i) evasion $\text{CO}_2\text{-C}$ was generally $\sim 5\text{--}6$ years younger than DOC-C (with the exception of the peak flood when ages were comparable), (ii) that there was a shift to the release of older (but still post-bomb) $\text{CO}_2\text{-C}$ during the peak flood event, and (iii) like DOC-C the youngest $\text{CO}_2\text{-C}$ was associated with the lowest flow and highest streamwater temperatures at the end of the study period. The isotopic data therefore suggest that at the end of the study period when soils and waters became warmer, evasion CO_2 had a stronger contemporary biological signal, most likely linked to soil (root and/or microbial) respiration of C fixed within the previous year. The release of more ^{14}C enriched evasion $\text{CO}_2 \sim 1$ month earlier indicates that older CO_2 (6–11 years old) was being lost during the main spring snowmelt event. One possible explanation is that CO_2 stored within the snowpack, which reached concentrations up to 1800 ppmv (Dyson et al. 2011) and was preferentially released into the stream system during main flood event (Dinsmore et al. in press), was produced from the microbial decomposition of older SOM during the winter. When soils were warmer (end of the study period) the decomposer community switched back to more available recently fixed C. This could also explain why the pre-flood evasion $^{14}\text{CO}_2$ values are slightly older than the

post-flood samples. Additionally a slightly greater proportional contribution of atmospheric CO_2 in the post-flood evasion samples would also produce a more ^{14}C depleted sample, although clearly evasion CO_2 is at all times predominantly derived from decomposition of SOM. This is further supported by ^{13}C -enrichment of evasion CO_2 in the post-flood compared to the pre-flood period.

Comparison with other studies

Whilst the isotopic signature of evasion CO_2 has only been directly measured in one previous study (Billett et al. 2007) our results for DOC and POC are consistent with most of the published literature, which show that terrestrial DOC exported to streams and rivers is derived from recently fixed ($^{14}\text{C} > 100\%$ modern) C, with DOC relatively ^{14}C enriched (younger) compared to POC ($^{14}\text{C} < 100\%$ modern; Hedges et al. 1986). We compared the $\delta^{13}\text{C}$ and ^{14}C isotopic values from this study of streams draining forested peatlands at the end of the winter period, with DOC and evasion CO_2 values measured throughout the year from streams draining unforested UK peatlands (Billett et al. 2007). Whilst the isotopic data for DOC from the UK and Finland agree closely, the evasion CO_2 data are markedly different (Fig. 5). Almost all measurements of evasion CO_2 from UK peatland streams are more ^{13}C enriched,

Fig. 5 Comparison of $\delta^{13}\text{C}$ and ^{14}C of evaded CO_2 and DOC from the 2 peatland streams in E Finland with values from UK peatland streams (after Billett et al. 2007). All CO_2 evasion isotopic values have been corrected to account for non-ambient conditions in the collection chambers (see Billett and Garnett 2010)



with a greater range of $\delta^{13}\text{C}$ values. Likewise most of the UK sites are more ^{14}C depleted ($<100\%$ modern, i.e. older) compared to the 2 Finnish sites; collectively suggesting that weathering is likely to be a more important source of evasion CO_2 in the UK peatland catchments (Billett et al. 2007). In addition, anaerobic fermentation could contribute to a more ^{13}C enriched deep peat/groundwater CO_2 isotopic signal (Waldron et al. 1999). Using a correlative approach (generalized-additive modelling) Humborg et al. (2010) also demonstrated the importance of groundwater sources for aquatic CO_2 in streams (particularly during winter). The importance of deep peat/groundwater CO_2 sources is further supported by studies of concentration-discharge relationships during storms (Dinsmore and Billett 2008). Figure 5 also demonstrates a much closer connectivity in the isotopic signatures of evasion CO_2 and DOC in the Finnish sites compared to the UK sites, where source and age differ markedly. This could be explained by the highly acidic nature of the underlying parent material at the 2 sites in Finland (Ahtiainen et al. 1988), where carbonate weathering is minimal or non-existent and cation concentrations are low (Dinsmore et al. in press). Additionally, it is interesting to note that the peatland sites in Finland were forested, whereas those in the UK were unforested.

The isotopic data therefore strongly suggest that the cycling of different forms of C at the Finnish sites was more closely linked because the radiocarbon content of DOC and evasion CO_2 were both significantly correlated and isotopically young as well as of similar source. We speculate this could be a feature of more rapid turnover of C in forested peatlands compared to non-forested systems and supports the findings of Dinsmore et al. (in press) for a common source of DOC and evasion CO_2 in the 2 Finnish catchments. More rapid turnover of near-surface biogenic C would also tend to mask any isotopic evidence of deeper groundwater CO_2 sources in these highly acidic, organic rich peatland streams.

Conclusions

We found the hypothesis that winter freezing switches off turnover of recently fixed C to be untrue, in terms of the isotopic measurements of evasion CO_2 . DOC released in streams was on average $\sim 5\text{--}6$ years older than evasion CO_2 , suggesting that gas phase C is more

mobile in frozen soils than dissolved C. This is consistent with more rapid diffusive movement of C in peat in the gaseous phase, compared to C transported by mass flow (Clymo and Bryant 2008). Although there was evidence for the release of older (post-bomb) evasion CO_2 during the spring snowmelt period, our results provide no evidence to suggest that much older (pre-bomb) soil C (or groundwater derived inorganic C) was stored during the winter and released into streams before the main spring snowmelt period. During the winter it seems likely that the isotopic signature of streams draining peatlands forested with conifers is affected by recently fixed C (rather than aged C) released as CO_2 and DOC from active root systems below the frozen soil surface. Spring runoff appears to be dominated by near-surface flow and overwhelmingly carries modern CO_2 and DOC. Progressive changes in the stable isotope signature of evasion CO_2 during the sampling period reflect decreasing concentrations of winter accumulated, soil derived CO_2 and a corresponding increase in the proportion of atmospheric CO_2 , as the freshwater system “reconnects” with the atmosphere. We also found that DOC and evasion CO_2 released from the drained peatland site was slightly younger in age (more ^{14}C depleted) than the undrained site and evasion CO_2 more ^{13}C enriched, suggesting a closer link to atmospheric CO_2 at the drained site. These differences are however small. The isotopic data imply that not only is the turnover of C more rapid from the 2 Finnish forested peatland sites compared to UK non-forested peatlands, but there is greater connectivity between the cycling of DOC and CO_2 . Dual isotope analysis of evasion CO_2 (in contrast to DOC) therefore provides a highly sensitive way of interpreting short-term (and potentially long-term) changes in C transport in aquatic systems. In this case we identified a clear contemporary plant growth signal in streams draining forested peatlands at the onset of the boreal summer.

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